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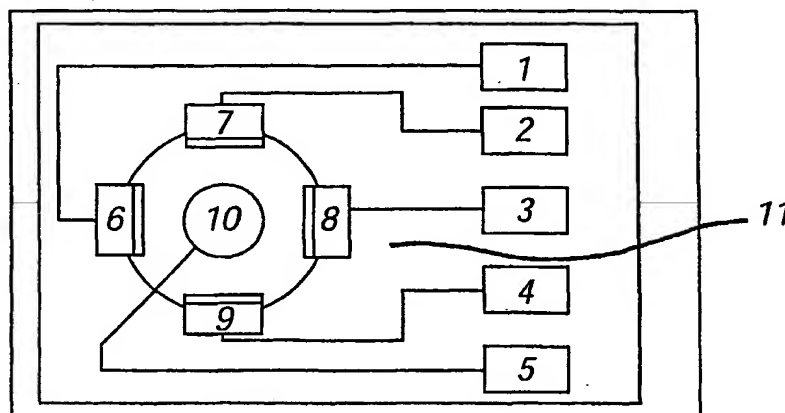
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(54) Title: APPARATUS AND METHOD FOR APPLYING DIAMOND-LIKE CARBON COATINGS



(57) Abstract: The invention relates to a coating and apparatus and method for applying the same, said coating including Diamond Like Carbon (DLC) applied by chemical vapour deposition using a pulsed DC biased power supply, typically having an initial metal layer and followed by a transitional metal carbide layer and a DLC layer. The depths and transitions between the materials can be selected to suit requirements. The apparatus also includes the use of an arrangement with at least one electrode with an RF power supply and the selective control of the power supplies to the electrode and substrates is used to improve the efficiency of application.

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Apparatus and Method for Applying Diamond-Like Carbon Coatings

The invention to which this application relates is particularly although not necessarily exclusively, to apparatus and a method for the application of a type of coating known as a diamond-like carbon coating to a substrate surface.

Diamond-like carbon coatings are well known and properties of the same such as the hardness, wear resistance and the like are known. The current invention relates to an improvement in the application of a diamond-like carbon coating which further enhances the characteristics of the coating over and above the conventional coatings of this type. A further type of carbon coating is one which has a graphite-like structure which has a lower friction and much better wear resistance than diamond-like carbon coatings which include metal and retain the advantageous properties at high loads in that they have had exceptional load bearing capacity. One such coating is described in the applicant's co-pending application EP-1036208.

There are a number of different known ways of applying diamond-like carbon coatings to a substrate surface, each of which are used commercially with varying degrees of success and for particular applications. Thus particular types of application may be used to suit specific purposes and/or end uses of articles including the coating.

Typically, it is known to be possible to deposit a carbon coating with a diamond-like structure (hereinafter referred to as a diamond-like carbon coating), by creating a glow discharge to a substrate to be coated in a controlled atmosphere containing a hydrocarbon gas. The glow discharge causes a breakdown of the hydrocarbon gas and the carbon from said gas is deposited

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on the substrate. One well known embodiment of this method is to use an RF discharge on the substrate as described in the Holland and Ojha publication in the Journal, Vacuum 26, page 53 1975.

There are many variations on this method and, by controlling the deposition parameters, the diamond-like carbon coating which is achieved can have variations in characteristics and properties to suit specific uses. Indeed, discharges other than an RF discharge can be used, the power and voltage applied can be varied, differing hydrocarbon gases can be used and/or mixed with other gases such as argon and hydrogen and thus it will be seen that the variation of various parameters of the coating method can be controlled to provide the required end result.

While the application of this type of coating in accordance with this method can be successful in terms of the hardness of the coating, the diamond-like carbon coatings have been found to be relatively brittle and achieving adhesion of the coating to the substrate surface is found to be difficult to achieve to any significant degree.

Conventionally, in order to attempt to overcome these problems, modifications to the deposition procedure and method have been made. One change has been to deposit a small amount of metal along with the carbon from the gas. One such method is described in the document Grischke Bewilogua and Dimigen "Materials and Manufacturing Processes 8(4&5) 407 1993". The presence of the metal is found to reduce the internal stresses of the coating when applied and, as a result, produces a less brittle coating. However it also reduces the hardness of the coating.

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For the application of diamond-like coatings containing metal in a coating chamber, RF power is applied to the substrate to be coated and this serves to break down the hydrocarbon gas in the vicinity of the substrate and so deposit the diamond-like coating on the substrate surface. At the same time, metal is deposited by sputtering from a metal target onto the substrate and hence the coating which is achieved has a diamond-like carbon coating property with metal incorporated therein. However, there are known to be a number of disadvantages to this method in that it is necessary to use a matching network and tuner to reduce the reflected power from the RF power supply and, for large scale deposition systems, the RF power supply, with the associated matching network and tuner, are expensive and have reliability problems as well as convenience problems when compared to the use of DC power supplies.

For example, it is necessary to provide extensive shielding to prevent damaging leakage of the RF power in the chamber and the matching network required has to be able to provide a wide range of impedance values corresponding to the wide range of substrate loads in the coating chamber and so RF power supply deposition methods are conventionally regarded as being inconvenient for a large scale coating system. Furthermore, when RF power is applied to the substrate there is no ability to control, independently, two deposition parameters, namely the voltage applied to the substrates and the ion current drawn by the substrates.

Despite the disadvantages, RF power is typically used, as the diamond-like carbon coatings are electrically insulating. Conventionally, if DC power is to be used then the coating is required to be conducting. This can be achieved by including a higher metal content in the coating but this type of coating has

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less desirable properties than the RF deposited metal containing Diamond Like Coating (DLC).

The aim of the present invention is to provide an improved method and apparatus for depositing diamond-like carbon coatings with tribological properties superior to conventional diamond-like carbon coatings and preferably which have similar characteristics to those of the graphite-like structure carbon coatings.

In a first aspect of the invention there is provided a method for the formation of a diamond-like carbon coating on at least one substrate, said method comprising the steps of supplying a hydrocarbon gas into the vicinity of the substrate, applying a pulsed DC biased power supply to the substrate to cause the break up of the hydrocarbon gas structure and the application of carbon from said gas onto said substrate to form a diamond-like carbon coating thereon.

In one embodiment, the method can further include the step of depositing a metal onto said substrate surface so as to form a diamond-like carbon coating including a metal therein. Typically the metal is deposited simultaneously with the deposition of the carbon from the hydrocarbon gas, but, as required, the application of the metal can be controlled separately and independently from the carbon, thereby allowing, if required, carbon only coatings or portions of the coatings to be applied.

Typically the hydrocarbon gas is introduced into a controlled deposition chamber in which the substrates are held.

Preferably, the pulsed DC bias voltage applied to the substrates and the ion current drawn by the substrates are independently controlled. In one embodiment the independent control is

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achieved by the utilisation of at least one electrode in the deposition chamber in which the substrate is located. Typically an RF power supply is connected to said electrode to enhance the discharge of the pulsed DC bias on the substrates to change the impedance of the glow discharge.

In a further aspect of the invention, there is provided apparatus for the deposition of a diamond-like carbon coating onto a substrate, said apparatus comprising a deposition chamber in which the at least one substrate is mounted, a means for introducing hydrocarbon gas into said deposition chamber, at least one metal target, deposition means to allow the metal to be deposited onto said substrate, and a means for applying a pulsed DC bias voltage to said at least one substrate and characterised in that the at least one electrode is positioned in the deposition chamber and acted upon by an RF power supply.

In one embodiment the apparatus includes two or more electrodes which are acted upon by the RF power supply.

In further aspects of the invention there are provided a coating and an article including a coating, said coating formed using the method and/or apparatus as herein described.

A specific embodiment of the invention is now described with reference to the accompanying drawings, wherein:-

Figure 1 illustrates a deposition apparatus in accordance with one embodiment of the invention;

Figures 2A and B illustrate performance characteristics of coating produced in accordance with one embodiment of the invention tested using a pin on disc test; and

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Figures 3A and B illustrate characteristics of a coating applied in accordance with the embodiment of Figures 2A and B tested using a reciprocating test.

Referring firstly to Figure 1, there is illustrated one embodiment of a sputter ion plating system adapted in accordance with this invention and including sputter magnetrons and at least one electrode in a closed field in a coating chamber 11 as a closed field sputter ion plating system. The magnetron sputtering part of the apparatus is similar to that described in detail in the applicant's patent GB2258347.

Figure 1 illustrates the system in schematic manner with there being provided a DC power supply 1 connected to the magnetron 6. In addition, there is also provided an RF power supply 2 connected to electrode 7 in accordance with the invention. A further DC power supply 3 is provided for magnetron 8 and a DC supply 4 is provided for magnetron 9. A pulsed DC power supply 5 is provided to apply the pulsed DC power supply to the substrates on the substrate holder 10.

In this example the magnetrons are provided with chromium targets to allow the application of chromium as part of the coating, mainly to provide the adhesion layer with the substrate, but also as a possibility of including the metal as a part of the carbon coating as will be described.

In this embodiment, a hydrocarbon gas is introduced into the deposition chamber and in this case the gas is butane. Other hydrocarbon gasses can be used and parameters such as rates of deposition and thickness of the coatings in different stages of deposition can be varied to suit particular requirements although, in terms of changing the properties of the coating, any

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parameter changes are performed gradually in order to avoid abrupt changes in the mechanical properties of the coating.

The electrode with RF power supply is provided and operated in a manner which will now be described, to allow the enhancement of the plasma created in the vicinity of the substrates and hence improve the characteristics of the coating which is applied.

In operation, the RF power is applied to the electrode to enhance the discharge of the pulsed DC bias on the substrate, to change the impedance of the glow discharge of the substrate on the substrate holder 10. The ability to change the impedance of the pulsed DC discharge means that, after setting the voltage of the pulsed DC power applied to the substrates, the ion current drawn by the substrates is varied by altering the level of RF power 2 applied to the electrode 7. Thus, there is provided independent control of the bias voltage and current by changing the RF power applied to the electrode 7. The RF power applied to the electrode has none of the disadvantages of the conventional systems for the application of RF power to the substrates as only a relatively low RF power is applied, even for a large scale coating system. Low RF power supplies are more reliable than the larger level RF power supplies and as a result the matching network for the power supply uses more robust and cheaper components. Thus, the electrode is provided of constant size and shape and the matching network and tuner, once set, needs no further adjustment.

A specific embodiment of the invention is now provided and, the power levels herein given relate to apparatus with a chamber of 850mm height and 750mm diameter with the magnetron electrodes 700mm long and 175mm wide.

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The operating method which is performed involves the following steps. Firstly, the deposition chamber 11 is pumped to below 5×10^{-5} torr pressure whereupon argon is introduced into the chamber through a mass flow valve and set at around 30 sccm which results in a chamber pressure of around 3×10^{-3} torr. The pulsed DC bias supply 5 is connected to the typically rotatable substrate holder with the substrates energised and set at about -400V. A pulse frequency of about 250 μ s and a pulse width of about 1.5ns are used although these settings can be varied to suit particular coating requirements.

The DC power supplies 1,3,4 are connected to the magnetrons 6,8,9 respectively and energised and set to about 0.6 Amps with the above conditions resulting in efficient ion cleaning of the substrates and typically lasting for approximately 20 minutes.

When the cleaning process is completed the voltage of the power supply is reduced to about -100 Volts and the current settings of the DC supplies increased to 6 Amps. During this time, which lasts approximately 5 minutes, there is applied from the magnetrons a metal to form a metallic layer, typically but not exclusively of chromium to a depth of approximately 0.1 to 0.2 μ m. This acts as an adhesion layer between the coating and substrate surface.

When the application of the metal layer is completed, the voltage applied to the substrates (10) is reduced to about -40 Volts and butane is introduced into the chamber, the level of which is controlled by optical emission close loop feedback to a piezoelectric valve. The percentage of the metal which is to be used to form part of the coating is set at 60% and the current settings are maintained at 6 Amps. During this stage chromium is deposited onto the substrates along with carbon from the butane gas. This stage typically lasts around 45 minutes and

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results in a chromium carbide layer of approximately $1\mu\text{m}$ depth. At the end of this stage, butane is introduced through a mass flow valve and the level of butane is increased from zero to around 30 sccm, typically over a period of 20 minutes and during this time the piezoelectric valve closes automatically due to the input of butane through the mass flow valve. When the maximum gas flow rate has been reached, the parameters remain constant and at this time the RF power supply 2 which is connected to the electrode 7 is energised. The RF power which is applied is increased to 300 Watts over a period of at least 30 minutes and during this period of time the DC currents to the magnetron 6, 8, 9 applied are reduced to zero so that there is no metal deposition and hence no metal content in the final or outer layer of the coating, and the bias voltage is increased to around to -100 Volts. This final stage lasts approximately 60 minutes and results in a layer thickness of about $1\mu\text{m}$. It is possible to maintain some power to the targets in the final stage if it is desired that the outer layer of the coating includes some metal.

As a result of following the process so described, a coating is achieved on the substrate which possesses excellent structure and properties and, if the final layer is greater than approximately $0.8\mu\text{m}$ the coating is black in appearance, is electrically insulating and smooth. The structure of the coating itself is amorphous inasmuch that the metal and carbon can be, if required, formed as an integral coating, although typically including no or less quantities of metal than that of carbon. This composition can be adjusted to suit specific requirements. Typically the metal layer is always first applied to improve adhesion of the coating to the substrate surface.

The example as herein described therefore provides an excellent coating to suit many purposes. However it should be

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appreciated that the coating characteristics can be altered to suit requirements by adjustment of certain parameters of the coating system. For example, a higher bias voltage level produces a coating with a higher hardness level than that of the example given.

In one embodiment, typical thicknesses of the various stages of the coating are as follows:-

Metal (Chromium) interlayer on substrate of approximately $0.1\mu\text{m}$

Metal (Chromium) Carbide of approximately $1\mu\text{m}$

Ramp layer metal (chromium) carbide grading to DLC of approximately $0.7\mu\text{m}$

DLC layer containing no or reduced metal content of approximately $1\mu\text{m}$

The hardness of the coating is dependent on the exact deposition parameters but in order to give optimum tribological properties at very high loading, the parameters described can be used and the coating has a plastic hardness of about $1,400\text{kg}/\text{mm}^2$.

It should be added that it is preferred that in the transition between metal carbide and DLC layers, at least, there is provided a transition period during which there is a gradual adjustment of parameters so as to enable a transitional amorphous coating to be achieved and therefore limit or minimise any stresses or fractures in the coating.

The adhesion of the coating is also an important feature and is measured by a scratch test using a $200\mu\text{m}$ diamond. The first adhesion failure occurs above 60N with some minor chipping recorded at 30N to indicate some cohesion failure.

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The most remarkable feature of this coating is its very low wear and extremely high load and typical results from a pin and on disc test are illustrated in Figures 2a and b.

In these figures the coating 12 was deposited on an M42 high speed steel substrate hardened to 850VHN. The pin used was a 5mm diameter WC/Co and the tests were carried out in air at about 40% relative humidity. Figures 2a and b show the specific wear rate obtained from the measurement of the coating thickness in the wear track 14 and outside the wear track 16 using a ball crater taper section method. The specific wear rate obtained of $1.5 \times 10^{-17} \text{m}^3/\text{Nm}$ is lower than the wear rate of any conventional DLC known to have been tested. Furthermore, no other DLC will withstand an 80N load and will usually fail within about 1 minute of application of the load.

A bi-directional wear test performed on the coating using a 5mm WC/Co ball at 80N load, with 150mm/min. linear of velocity, 2mm linear displacement, and over 10,000 cycles and tests in air of 20°C and 40%RH provided the results shown in Figures 3a and b. Further reciprocating wear tests, but using 5mm balls of soft metals, as the counterface pin (replacing the WC/Co ball) indicated low galling and pick-up from the soft metals. Metals tested include aluminium, copper, titanium, gold and silver.

Figure 2b shows a wear track and friction trace 18 from a pin on disc test. Figure 3b shows a wear track and friction trace 20 from a reciprocating wear test.

The examples of the method and apparatus of the invention described are provided to illustrate the advantageous features of the invention but the examples do not restrict the wider scope of the invention such that alteration to the method parameters

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can be made to generate coatings within the inventive concept but having specified properties. Furthermore the apparatus can include, particularly for larger systems, two or more RF electrodes to improve the efficiency of the same.

The low friction and wear properties make the coating suitable for a large range of applications such as forming tools, dies, moulds, punches, for non-ferrous work piece materials in particular; cutting tools, drills, milling cutters, taps for non-ferrous work piece materials, cold extrusion dies, protecting motor engine parts, gudgeon pins, cam followers, piston rings, injector nozzles, vacuum pickup nozzles and the coating is also suitable for use as a decorative shiny black coating for items such as watch straps.

The present method therefore successfully addresses the disadvantages and inconvenience of conventional RF methods for applying DLC coatings and allows the independent control of the bias voltage and bias ion current. High quality electrically insulating DLC coatings can be deposited without using RF bias on the substrate and, because independent control of the bias voltage and ion current is possible, the properties of the coating can be optimised and are much improved as compared to previous conventional metal containing or non-metal containing DLC coatings.

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Claims

1. A method for the formation of a diamond-like carbon coating on at least one substrate, said method comprising the steps of supplying a hydrocarbon gas into the vicinity of the substrate, applying a pulsed DC biased power supply to the substrate to cause the break up of the hydrocarbon gas structure and the application of carbon from said gas onto said substrate to form a diamond-like carbon coating thereon.
2. A method according to claim 1 characterised in that a metal is deposited onto said substrate surface to form a diamond-like carbon coating including a metal therein.
3. A method according to claim 2 characterised in that the metal is deposited simultaneously with the deposition of the carbon from the hydrocarbon gas.
4. A method according to claim 2 or 3 characterised in that the deposition of the metal is controlled separately and independently from the control means for the application of the carbon.
5. A method according to claim 1 characterised in that the hydrocarbon gas is introduced into a controlled deposition chamber in which the substrates are held, firstly in conjunction with the deposition of metal and thereafter with no metal deposition.
6. A method according to claim 1 characterised in that the pulsed DC bias voltage applied to the substrates and the ion current drawn by the substrates are independently controllable.

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7. A method according to claim 6 characterised in that the independent control is achieved by the selective application of an RF power supply to at least one electrode in the deposition chamber in which the at least one substrate is located.

8. A method according to claim 7 characterised in that an RF power supply is connected to the electrode to enhance the discharge of the pulsed DC bias on the substrates to change the impedance of the glow discharge.

9. Apparatus for the deposition of a diamond-like carbon coating onto a substrate, said apparatus comprising a deposition chamber in which the at least one substrate is mounted, a means for introducing hydrocarbon gas into said deposition chamber, at least one metal target and deposition means to allow metal from the target to be deposited onto said substrate and a means for applying a pulsed DC bias voltage to said at least one substrate and characterised in that at least one electrode is positioned in the deposition chamber and an RF power supply connected thereto.

10. Apparatus according to claim 9 characterised in that the apparatus includes two or more electrodes which are acted upon by an RF power supply.

11. Apparatus according to claim 9 characterised in that a DC power supply is provided to the deposition means and the application of the DC power supply and RF supply is selective during the application of the coating.

12. A coating formed using the method of claims 1-8 and/or apparatus of claims 9-11, said coating including at least a layer of carbon containing a metal.

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13. A coating according to claim 12 characterised in that the coating includes a layer of metal, metal carbide and DLC

14. A coating according to claim 12 characterised in that the coating is substantially amorphous and includes transitional phases as the thickness increases between the metal carbide and LC material.

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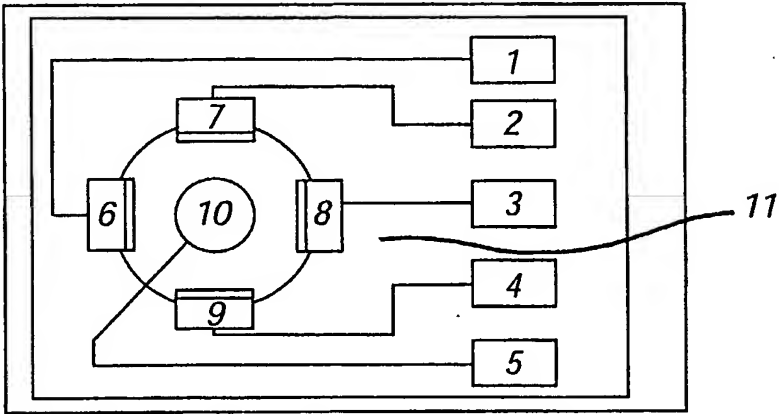
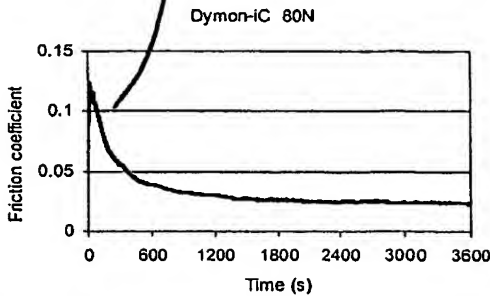
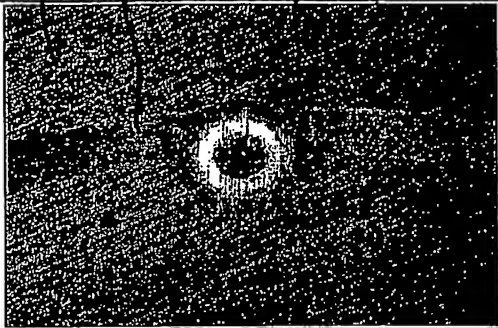


FIG. 1

16 14 12 18
80N load, Ø8mm track / 477rpm, linear speed 200mm/s, testing time 60 minutes



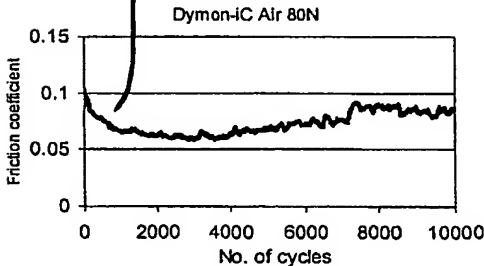
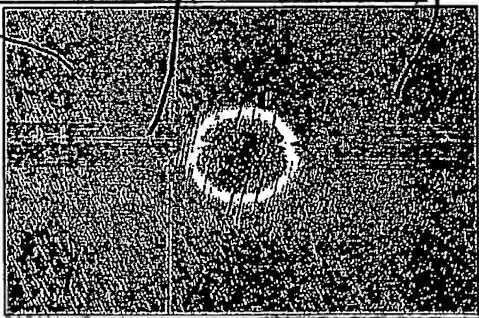
1Wear - 0.3µm, Track width - 230µm

Specific Wear Rate - 1.5×10^{-17}
 m^3/Nm

Figure 2a

Figure 2b

16 14 12 20
Tested in Air (20°C, 40%RH)



Wear - 0.6µm, Track width - 204µm

Specific Wear Rate - 3.8×10^{-17}
 m^3/Nm

Figure 3a

Figure 3b

INTERNATIONAL SEARCH REPORT		Intl. Application No PCT/GB 03/01078
A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C23C16/26 C23C16/517 C23C16/02 H01J37/32		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C23C H01J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 10688 A (DOI AKIRA ;IZUMI YOSHIHIRO (JP); KUWAHARA HAJIME (JP); NAKAHIGASHI) 20 March 1997 (1997-03-20) -& US 6 465 057 B1 15 October 2002 (2002-10-15) column 11, line 66 -column 12, line 31; claims; figure 7 column 6, line 15 - line 29 --- -/--	1-8, 12-14
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
<p>* Special categories of cited documents :</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p>		
Date of the actual completion of the international search 25 June 2003		Date of mailing of the international search report 10/07/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Mauger, J

INTERNATIONAL SEARCH REPORT

Int. Patent Application No
PCT/GB 03/01078

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MICHLER T ET AL: "DLC films deposited by bipolar pulsed DC PACVD" DIAMOND AND RELATED MATERIALS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 7, no. 2-5, 1 February 1998 (1998-02-01), pages 459-462, XP004115085 ISSN: 0925-9635 Section 2. "Experimental details" figure 1 -----	1-5, 12-14
A	WO 99 27893 A (CAMINO DIDIER ;TEER COATINGS LTD (GB); JONES ANDREW HARRY SPENCER) 10 June 1999 (1999-06-10) page 12, line 21 -page 18, line 3; claims; figure 1 page 5, line 16 - line 21 & EP 1 036 208 A 20 September 2000 (2000-09-20) cited in the application -----	1-14
A	MONAGHAN D P ET AL: "ION-ASSISTED CVD OF GRADED DIAMOND LIKE CARBON (DLC) BASED COATINGS" JOURNAL DE PHYSIQUE IV, EDITIONS DE PHYSIQUE. LES ULIS CEDEX, FR, vol. 3, no. 8, 1 August 1993 (1993-08-01), pages 579-587, XP000602428 ISSN: 1155-4339 the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Int'l nal Application No
PCT/GB 03/01078

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9710688	A	20-03-1997	JP 3119172 B2	18-12-2000
			JP 9137273 A	27-05-1997
			CA 2205221 A1	20-03-1997
			WO 9710688 A1	20-03-1997
			US 6465057 B1	15-10-2002
			US 2002039626 A1	04-04-2002
WO 9927893	A	10-06-1999	AU 1344399 A	16-06-1999
			EP 1036208 A2	20-09-2000
			WO 9927893 A2	10-06-1999
			GB 2331998 A ,B	09-06-1999